SURFACE CHEMISTRY

ADSORPTION

LECTURE-4

INTRODUCTION TO MOLECULAR ADSORPTION

The phenomenon of attracting and retaining the molecules of a substance on the surface is called *adsorption*. The substance adsorbed on the surface is called *adsorbate* and the substance on which it is adsorbed is called *adsorbent*.

The adsorption of molecules on a surface is a necessary prerequisite for any surface mediated chemical process. In the case of a surface catalysed reactions, the whole process consists of five basic steps:

1. Diffusion of reactants to the active surface.
2. Adsorption of one or more reactants onto the surface.
3. Surface reaction.
4. Desorption of products from the surface.
5. Diffusion of products away from the surface.

The above scheme not only emphasises the importance of the adsorption process but also its reverse, namely desorption.

Some common terminology

Substrate: Frequently used to describe the solid surface onto which adsorption can occur; the substrate is also occasionally referred to as the *adsorbent*.

Adsorbate: The general term for the atomic or molecular species, which are adsorbed (or are capable of being adsorbed) onto the substrate.

Adsorption: The process in which a molecule is adsorbed onto a surface of another phase.

Coverage: A measure of the extent of adsorption of species onto a surface (unfortunately this is defined in more than one way), usually denoted by the symbol θ.

How do molecules bond to surfaces?

There are two principal modes of adsorption of molecules on surfaces:

(i) Physical adsorption (Physisorption).

(ii) Chemical adsorption (chemisorption).

(i) Physical adsorption (Physisorption): The first type, known as physical adsorption is exhibited by all substances at low and moderately low temperatures in which bonding is only by weak van der Waals type forces. There is no significant redistribution of electron density in either the molecule or at the substrate surface. It is characterized by low heats of adsorption, about 5— 40 kJ per mole of gas. The adsorption of hydrogen or oxygen on charcoal is an example of physical adsorption.

(ii) Chemical adsorption (Chemisorption): In this type of adsorption a chemical bond, involving substantial rearrangement of electron density, is formed between the adsorbate and substrate. The nature of this bond may lie anywhere between the extremes of virtually complete ionic or complete covalent character. Chemisorption is highly specific in character and depends on the chemical properties of the adsorbate and adsorbent. The heat of adsorption is quite high (40— 800 kJ per mole). For example, hydrogen is chemisorbed on nickel surface.

The differences between physisorption and chemisorption are given in Table 10.1

TABLE 10.1: Typical Characteristics of Adsorption Processes

	Chemisorption	*Physisorption*
Temperature range(over which adsorption occurs)	Virtually unlimited(but a given molecule may effectively adsorb only over a small range)	Near or below the condensation point of the gas(*e.g.*, Xe < 100 K, CO_2 < 200 K)
Forces	The forces operating in these cases are similar to those of a chemical bond	The forces operating in these cases are weak van der Waals forces
Adsorption enthalpy	Wide range (related to the chemical bond strength) – typically 40–800 kJ mol^{-1}	Related to factors like molecular mass and polarity but typically 5— 40 kJ mol^{-1} (*i.e.*, ~ heat of liquefaction)
Crystallographic specificity (variation between different surface planes of the same crystal)	Marked variation between crystal planes	Virtually independent of surface atomic geometry
Nature of adsorption	Often dissociative, may be irreversible	Non-dissociative reversible
Saturation uptake	Limited to one monolayer	Multilayer uptake possible
Kinetics of adsorption	1. Very variable, often an activated process 2. Adsorption increases with increasing temperature	1. Fast since it is a non–activated process 2. Adsorption decreases with increase of temperature

Adsorption isotherms

Adsorption of gases by solids is very common. It depends upon several factors:

(i) Surface area

The amount of a gas adsorbed, besides depending upon the nature of the gas, is greatly dependent on the surface area for a given mass of the adsorbent. It greatly increases with the increase in the surface area of the adsorbent. It is because of this reason most of the adsorbents are used in finely divided or porous form so as to provide large surface area.

(ii) Temperature

A decrease of temperature of the system leads to an increase of adsorption. At lower temperatures, the thermal energy is less and therefore more number of adsorbed molecules remain attached to the surface and hence the adsorption is more.

(iii) Pressure

At a constant temperature, the increase of pressure leads to large adsorption of gases. The extent of adsorption almost vary linearly with pressure up to a certain extent. After this further increase in pressure would not lead to an increase of adsorption and the extent of adsorption becomes independent of pressure.

At constant temperature, there exist some definite relationships between the amount of the gas adsorbed (x/m) and the equilibrium pressure. Such relations are known as adsorption isotherms. Five different general type of adsorption isotherms have been observed for the adsorption of gases on solids. These are shown in Fig. 10.1.
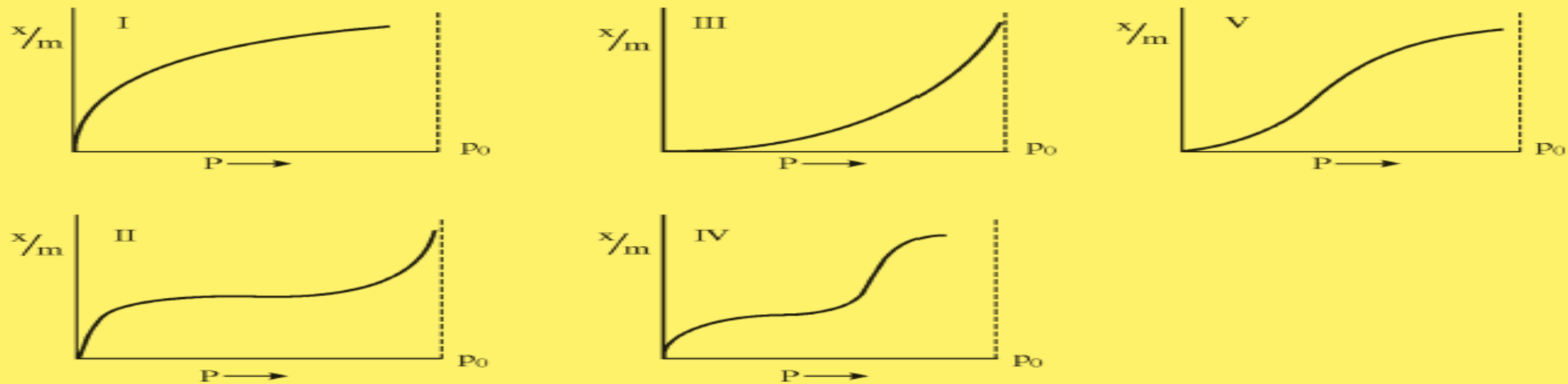
Fig. 10.1. Adsorption isotherms

Type I: Monolayer formation: Examples: N_2 at $-195°C$ on charcoal and O_2 at $-183°C$ on charcoal.

Type II: Examples: N_2 at $-195°C$ on iron catalyst, N_2 at $-195°C$ on silica gel.

Type III: Examples: Br_2 at $79°C$ on silica gel and I_2 at $79°C$ on silica gel.

Type IV: Examples: Benzene on Fe_2O_3 at $50°C$.

Type V: Examples: Water vapour at $100°C$ on charcoal.

In the case of chemisorption, only isotherms of type I are observed while for physical adsorption, all the five types of isotherms are possible.

Type I suggests the formation of unimolecular layer and the volume of the gas adsorbed reaches a limiting value with the increase of pressure of the system. Type II and III curves can be explained by considering the formation of several layers of physically adsorbed gaseous molecules. This multilayer adsorption occurs when the pressure of the gas is increased. Type IV and V adsorption isotherms are expected when actual condensation of the gas takes place in the small pores and capillaries of the adsorbent.

Adsorption isotherms of type I (in which the adsorption first increases rapidly with pressure and then remains nearly constant) were first explained by Freundlich and later improved by Langmuir.

Adsorption isotherms of the type II–V have been explained by BET equation discussed later in this chapter.

It is an explanation of adsorption isotherms of Type I. An empirical expression representing the isothermal variation of the extent of adsorption with pressure as suggested by Freundlich is

$$\frac{x}{m} = k \times p^{1/n} \qquad \qquad \ldots(10.1)$$

where 'x' is the mass of the gas adsorbed by m gram of the adsorbent at equilibrium pressure 'p' i.e., x/m is the amount of the gas adsorbed per gram of adsorbent, 'k' and 'n' are constants at a particular temperature and for a particular adsorbent and gas.

The above relationship is also called 'classical adsorption isotherm.' The quantity 1/n is generally less than 1 indicting that the amount of the gas adsorbed increases less rapidly than the pressure. The plots of the amount of the gas adsorbed against pressure (shown in Fig. 10.2 are called Freundlich adsorption isotherms).
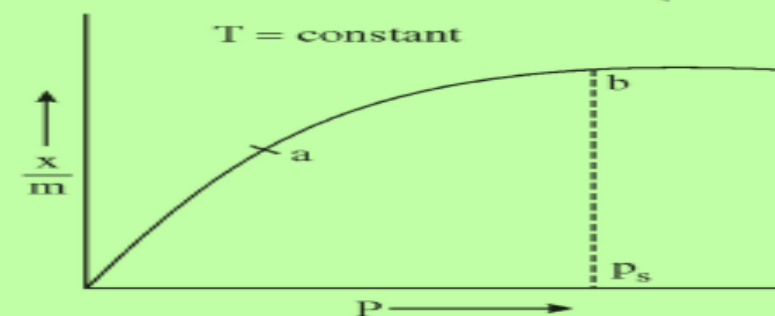

Fig. 10.2. Freundlich adsorption isotherm

At low pressures (say up to the point 'a') the graph is nearly linear. Hence for low pressures

$$\frac{x}{m} \propto p \qquad \qquad \ldots(10.2)$$

For very high pressures (say beyond the point 'b') the adsorption becomes almost independent of pressure i.e.,

$$\frac{x}{m} \propto p_s \qquad \qquad \ldots(10.3)$$

The state corresponding to the point 'b' is called the saturation state and the corresponding pressure p_s is called the saturation pressure. For intermediate pressure in between 'a' and 'b' obviously x/m will be proportional to 'p' raised to power lying between 0 and 1, i.e., fractions. Hence one may write

$$\frac{x}{m} \propto p^{1/n} \qquad \qquad \ldots(10.4)$$

or

$$\frac{x}{m} = k\,p^{1/n} \qquad \qquad \ldots(10.5)$$

The values of 'k' and 'n' for a given system can be determined by graphical method. On taking logarithm of both sides of the equation (10.5), one gets

$$\log\left(\frac{x}{m}\right) = \log k + \left(\frac{1}{n}\right)\log p \qquad \qquad \ldots(10.6)$$

Thus plot of log (x/m) against log p should be straight line with an intercept equal to log k and slope equal to (1/n) (Fig. 10.3).

For adsorption of solutes from solutions by solid adsorbents, Freundlich adsorption equation is written as

$$\frac{x}{m} = k \, C^{1/n} \qquad \ldots(10.7)$$

where 'x' is the amount of solute in grams adsorbed by 'm' grams of the adsorbent and C is equilibrium concentration of the solution.
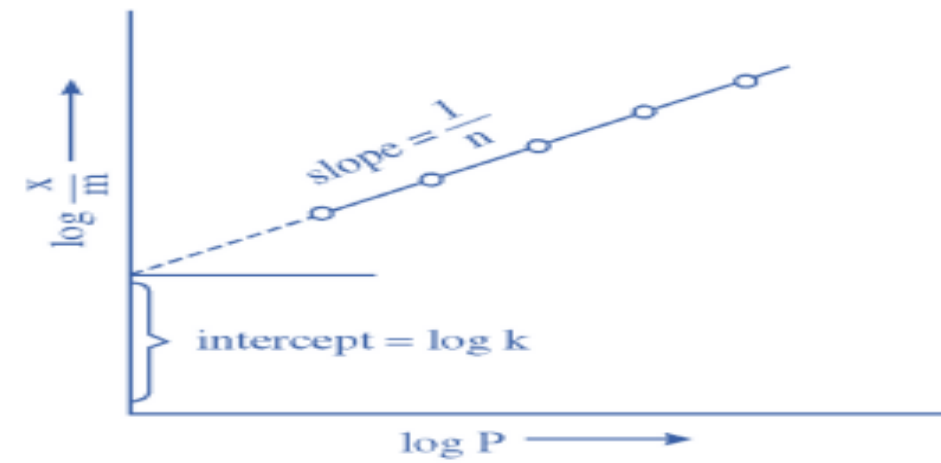

Fig. 10.3: Plot of log (x/m) vs log p.

THE LANGMUIR ADSORPTION ISOTHERM

Whenever a gas is in contact with a solid surface there will be an equilibrium between the molecules of the gas phase and the corresponding adsorbed species (molecules or atoms), bound to the surface of the solid. The position of this equilibrium depends upon a number of factors mentioned below:

1. The relative stabilities of the adsorbed and gas phase species involved.

2. The temperature of the system.

3. The pressure of the gas above the surface.

In general, factors (2) and (3) suggest that the *surface coverage* may be increased by raising the gas pressure but will be reduced if the surface temperature is raised.

Irving Langmuir in 1916 developed an isotherm to describe the pressure dependence of the extent of surface adsorption. He derived an expression for the variation of the extent of adsorption with pressure on the basis of following assumptions:

1. The adsorption is monolayer *i.e.*, only one layer of adsorption of gaseous molecules takes place.

2. All sites are equivalent and the surface is uniform.

3. The ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites. The adsorbed gaseous molecules do not interact with each other.
4. The surface of solid contains fixed number adsorption sites.
5. Each site can hold only one gaseous molecule and the heat of adsorption is constant for all the adsorption sites.

Fractional coverage (θ): The extent of surface coverage is normally expressed as the fractional coverage, θ

$$\theta = \frac{\text{Number of adsorption sites occupied}}{\text{Number of adsorption sites available}} \qquad \ldots(10.8)$$

This fractional coverage is often expressed in terms of volume as

$$\theta = \frac{V}{V_m}$$

where V is the volume of gas adsorbed at a particular temperature and pressure and V_m is the volume of the adsorbate (gas adsorbed) at sufficiently high pressure so that the surface is completely covered with a single (mono) layer of gaseous molecule. The rate of adsorption, $d\theta/dt$, is the rate of change of surface coverage which can be determined by observing the change of fractional coverage with time.

Derivation of Langmuir isotherm from equilibrium considerations

The adsorption process between unadsorbed gas phase molecules A, vacant surface sites S, and occupied surface sites SA involves a dynamic equilibrium and can be represented as

$$S + A \rightleftharpoons SA$$

Assuming that there are a fixed number of surface sites present on the surface, we may derive the Langmuir isotherm by considering that in this adsorption process there exists an equilibrium between the unadsorbed gas phase molecules (A), the vacant surface sites (S) and the species adsorbed on the surface (SA). Thus, for a non–dissociative (molecular) adsorption process, we may consider the adsorption to be represented by Fig. 10.4.

The above equilibrium process for the adsorption indicates that the forward reaction (adsorption) and backward reaction (desorption) can occur simultaneously. With the help of law of mass action, we may write

Fig. 10.4: Process of adsorption of gas molecules A on the surface

$$\text{Rate of adsorption} = k_a \,[S]\,[A] \qquad \qquad \ldots(10.9)$$
$$\text{Rate of desorption} = k_d \,[SA] \qquad \qquad \ldots(10.10)$$

At equilibrium, the rates of these two processes become equal. On equating them, we obtain the value of equilibrium constant for the equilibrium reaction. Thus, at equilibrium

$$k_a \,[S]\,[A] = k_d \,[SA]$$

or

$$\frac{k_a}{k_d} = \frac{[SA]}{[S][A]}$$

or

$$K = \frac{[SA]}{[S][A]} \qquad \qquad \ldots(10.11)$$
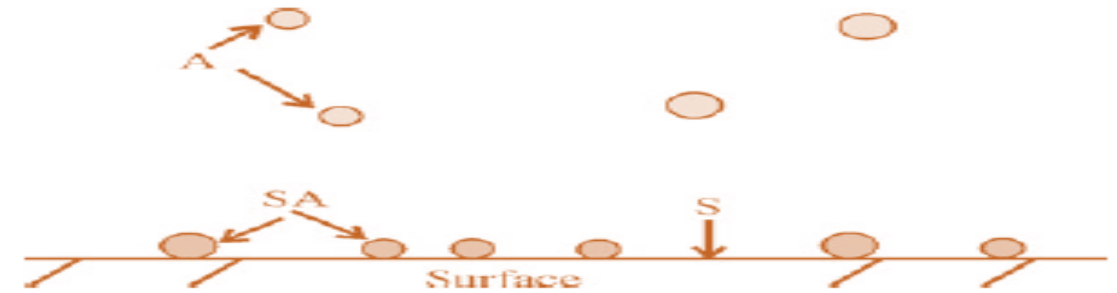
where

$$K = \frac{k_a}{k_d}$$

We may also note that:

- The concentration of adsorbed molecules [SA] is proportional to the surface coverage of adsorbed molecules, *i.e.*, proportional to θ (the fraction of the surface which is covered with gaseous molecules).
- The concentration of the vacant sites on the surface [S] is directly proportional to the number of vacant sites, *i.e.*, proportional to $(1 - \theta)$.
- The concentration of unadsorbed gaseous molecules [A] is directly proportional to the pressure of gas ρ.

Therefore, we can write

Rate of desorption of gas molecules $= k_d \theta$ (since the concentration of [SA] $\propto \theta$)

and

Rate of adsorption of gas molecules $= k_a \rho (1 - \theta)$

(since [S] $\propto 1 - \theta$ and [A] $\propto \rho$)

Therefore, at equilibrium, it follows that

$$k_a \rho (1 - \theta) = k_d \theta$$

Hence, it is also possible to define another equilibrium constant, K_1, as given below:

$$K_1 = \frac{\theta}{(1-\theta)\,\rho} \qquad\qquad ....(10.12)$$

where

$$K_1 = \frac{k_a}{k_d}$$

Rearrangement of Eq. (10.12) then gives the following expression for the pressure dependence of the surface coverage in the case of a simple reversible molecular adsorption process

$$\theta = \frac{K_1\,\rho}{1 + K_1\,\rho} \qquad\qquad ...(10.13)$$

This is the usual way of expressing the Langmuir adsorption isotherm which relates the extent of adsorption to the pressure of the gas at constant temperature. This is illustrated in Fig. 10.5. From this

figure it is clear that the extent of adsorption increases with increasing pressure. But of high pressure, it becomes constant.
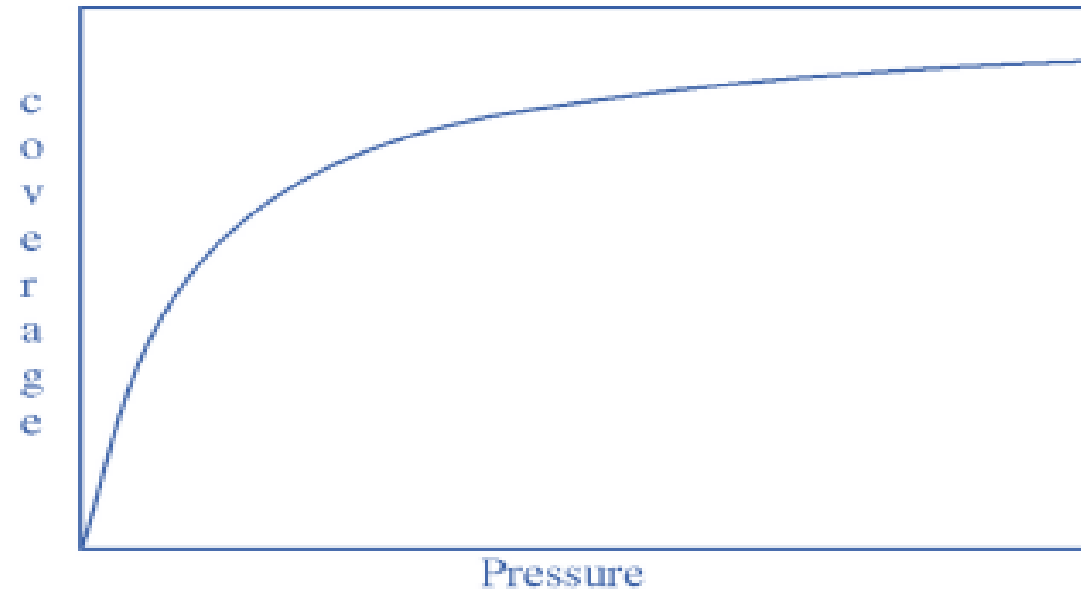
**Fig. 10.5:** The Langmuir adsorption isotherm

The Langmuir adsorption isotherm may also be expressed in terms of volume as $\left(\theta = \dfrac{V}{V_m} \right)$, so eq. (10.13) can be written as

$$\frac{P}{V} = \frac{1}{V_m}\frac{1}{K_1} + \frac{P}{V_m} \qquad \qquad ...(10.14)$$

If P / V is plotted against P, one gets a linear plot with slope equal to $1/V_m$ and an intercept equal to $\dfrac{1}{V_m K_1}$. Thus, the values of $V_m K_1$ can be calculated.

The different form of Langmuir adsorption isotherm for several values of equilibrium constant K_1 is also shown in Fig. 10.6.
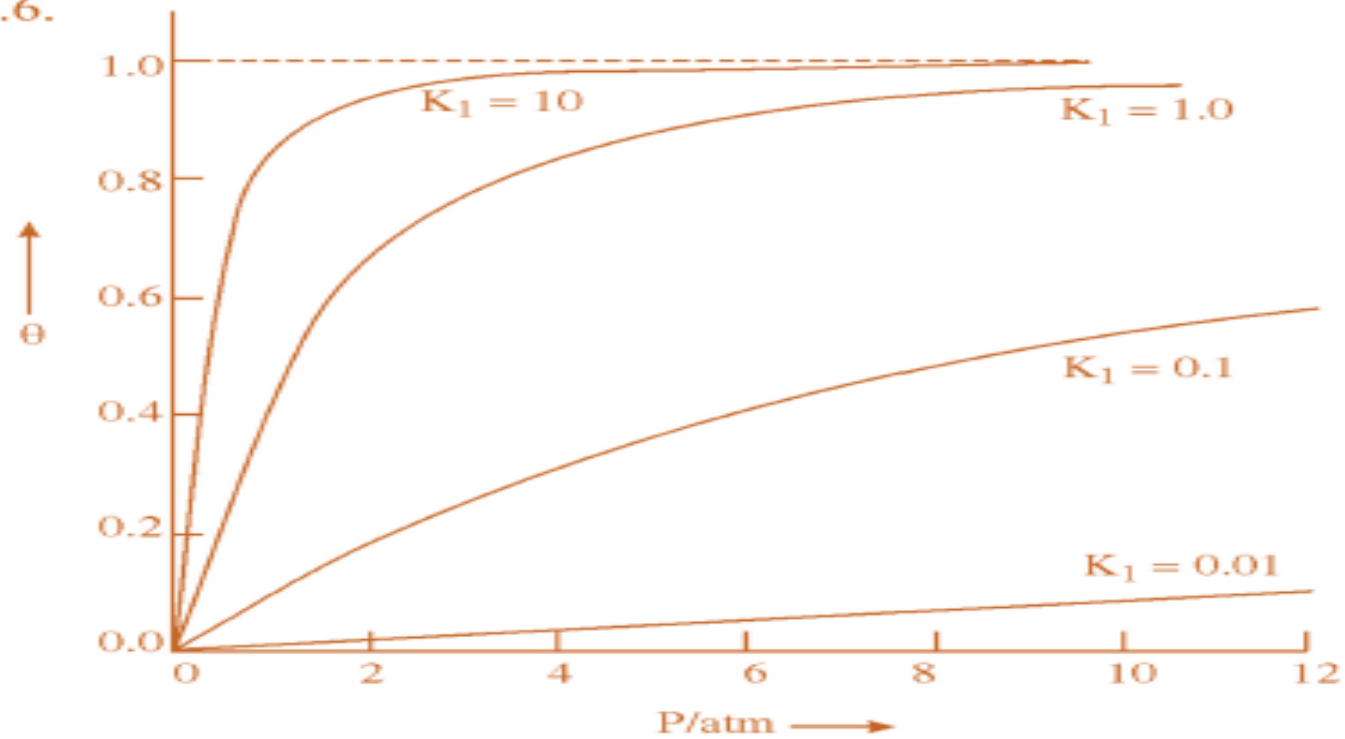

Fig. 10.6: The different forms of Langmuir isotherm at various value of K_1

Fig. 10.6 indicates that the surface coverage (θ) increase with pressure, and approaches unity only at very high pressures. Thus, two situations may arise:

(i) $\theta \to K_1 P$ at low pressure.

(ii) $\theta \to 1$ at high pressure.

A plot of equilibrium surface coverage obtained at various combinations of pressure and temperature is given in Fig. 10.7. This suggests that as the temperature is lowered the pressure required to achieve a particular equilibrium surface coverage decreases.
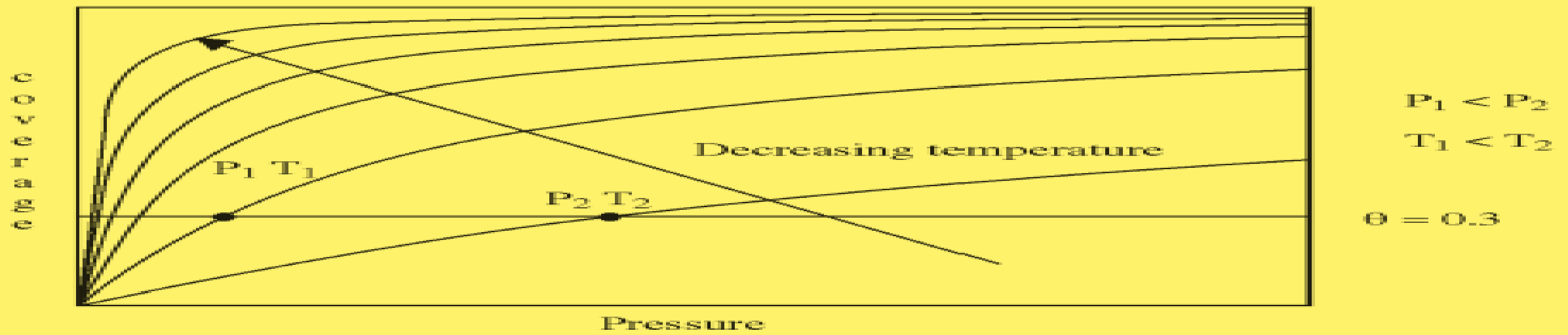
Fig. 10.7: Variation of surface coverage with pressure at different temperatures

$P_1 < P_2$

$T_1 < T_2$

$\theta = 0.3$

PHYSICAL SIGNIFICANCE OF CONSTANT K_1

The constant K_1, known as distribution coefficient, is actually equilibrium constant for the distribution of adsorbate between the surface and the gas phase. It is given by

$$K_1 = \frac{k_{desorption}}{k_{adsorption}} = \frac{\theta}{(1-\theta)} \frac{1}{P} \qquad \qquad ...(10.15)$$

At a given pressure the extent of adsorption is determined by the value of K_1: this in turn is dependent upon both the temperature (T) and the enthalpy (heat content) of adsorption. The magnitude of the adsorption enthalpy (a negative quantity itself) reflects the strength of binding of the adsorbate to the substrate. The value of K_1 is increased by:

1. A reduction in the system temperature.

2. An increase in the strength of adsorption.

The equilibrium constant K_1 may be used to determine the enthalpy of adsorption for a particular adsorbate/substrate system by studying the pressure–temperature dependence of the surface coverage. Experimentally same surface coverage can be determined at different pressures and temperatures as shown in Fig. 10.8. It is then possible to read of a number of pairs of values of pressure and
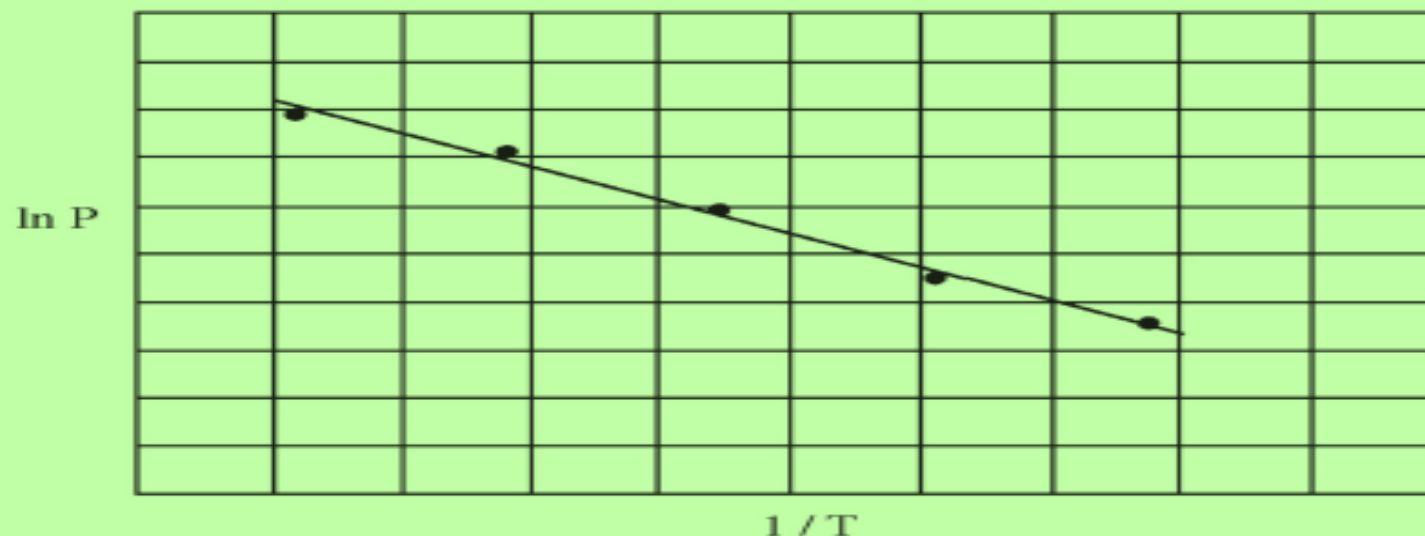
temperature which yield the same surface coverage. From these values by using the Clausius-Clapeyron equation

$$\left(\frac{\partial \ln P}{\partial (1/T)}\right)_\theta = \frac{\Delta H_{ads}}{R}$$
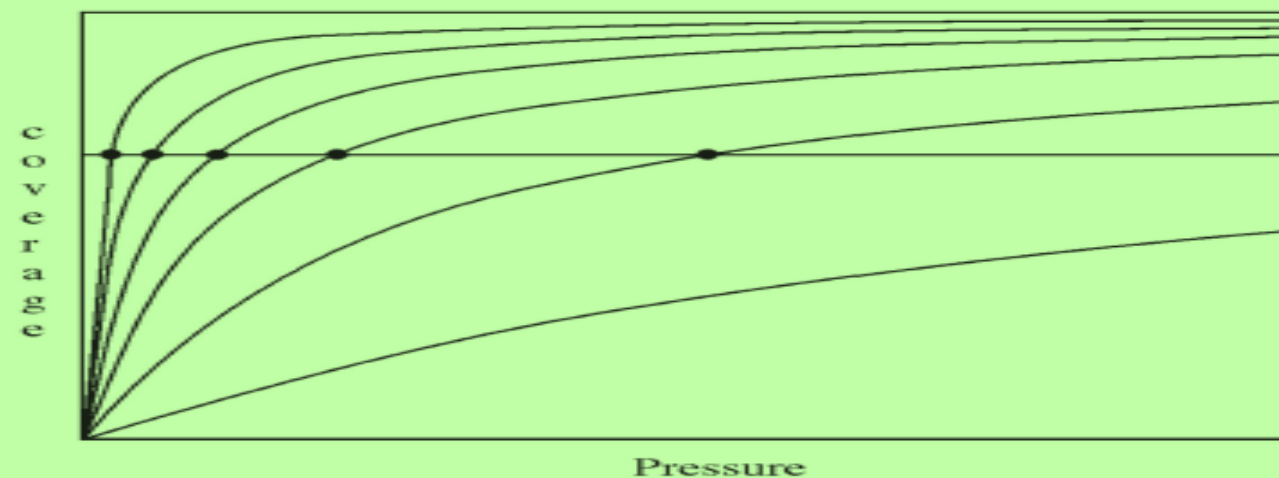

Fig. 10.8: Plot of pressure vs surface coverage

the enthalpy of adsorption can be obtained by plotting ln P vs 1 / T. The plot yields a straight line (Fig. 10.9). The slope of this line then gives the value of ΔH_{ads} / R. Thus ΔH_{ads} can be obtained.

Fig. 10.9: Plot of ln ρ vs 1 / T

The Langmuir theory of adsorption is valid for monomolecular layer adsorption lof gaseous molecules over solid surface. However, this theory does not take into consideration multimolecular layer adsorptions. Multilayer adsorption was proposed in 1938 by Brunauer, Emmett and Teller (commonly known as BET theory). The multilayer adsorption of gaseous nitrogen molecules on a solid surface is schematically shown in Fig.10.10.
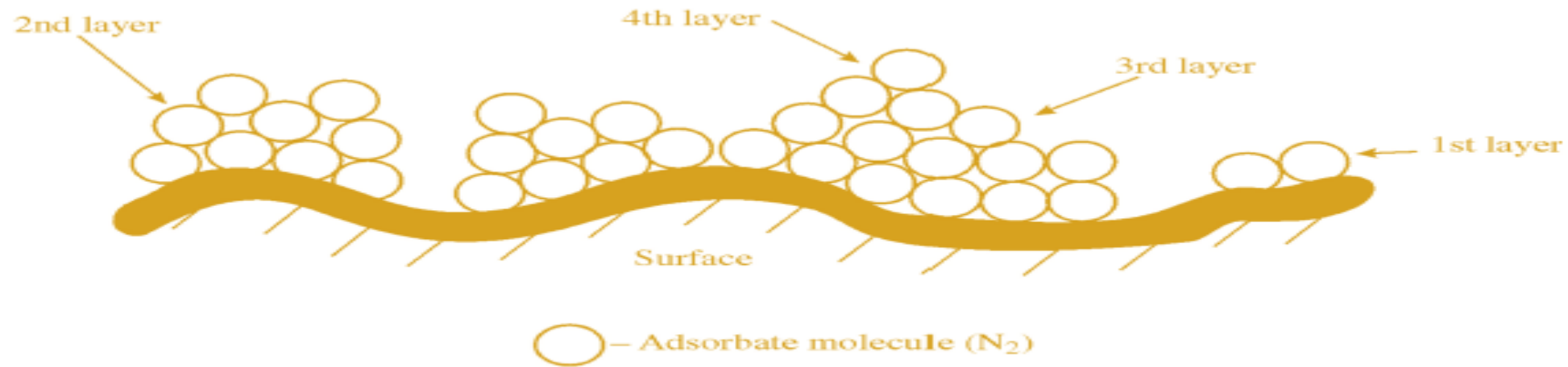
Fig. 10.10: Multilayer adsorption of N_2 molecules

The adsorption isotherms depicted in Fig. 10.10 have been interpreted by Brunauer, Emmett and Teller on the basis of formation of multimolecular layer. They derived a theoretical expression, known as BET adsorption isotherm, on a very similar lines adopted by Langmuir. The basic assumptions of BET theory are:

(i) The adsorbed surface may have a definite number of active centers, all of which are equivalent in energy and other characteristics.

(ii) The adsorption is multilayer.

(iii) Each molecule in the first layer is a possible center for adsorption and the formation of second layer; each molecule of the second layer is a possible center for the adsorption of third layer and so on.

(iv) There is no interaction between two the neighbouring adsorbed molecules in the first and subsequent layers.

(v) There is dynamic equilibrium between two successive layers. The rate of evaporation from a particular layer is equal to the rate of condensation on the preceding layer.

(vi) The heat of adsorption of molecules in second and subsequent layers is equal to heat of liquefaction E_L. The heat of adsorption in first layer being different.

The formation of multilayer adsorption as shown in Fig. 10.10 may be represented by following equilibria:

$$\left.\begin{array}{c} A + S \rightleftharpoons AS \\ A + AS \rightleftharpoons A_2S \\ A + A_2S \rightleftharpoons A_3S \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ A + A_{n-1}S \rightleftharpoons A_nS \end{array}\right\} \qquad \text{...(10.16)}$$

where, A, S, AS, A_2S etc. represent the unadsorbed gaseous molecule, the vacant site of the adsorbent surface, single molecule absorbed per vacant site, two molecules absorbed per vacant site and so on. The corresponding equilibrium constants of the various equilibria given by Eq. (10.16) are :

$$\left.\begin{array}{c} K_1' = \dfrac{[AS]}{[A]\ [S]} \\[2ex] K_2' = \dfrac{[A_2S]}{[A]\ [AS]} \\[2ex] K_3' = \dfrac{[A_3S]}{[A]\ [A_2S]} \\[2ex] \cdots\cdots\cdots\text{and so on} \end{array}\right\} \qquad \text{...(10.17)}$$

It is further assumed that,

(i) [A] $\propto$ pressure of the gas, i.e., [A] $\propto$ P

(ii) [S] $\propto$ fraction of the free surface i.e., [S] $\propto \theta_v$.

(iii) [AS] $\propto$ fraction of surface covered with one molecule adsorption, i.e., [AS] $\propto \theta_1$.

(iv) [A_2S] $\propto$ fraction of surface covered with two molecule adsorption, i.e, [A_2S] $\propto \theta_2$.

.........and so on

Hence, Eq. (10.17) can be represented as

$$K_1 = \frac{\theta_1}{P\,\theta_v}$$

$$K_2 = \frac{\theta_2}{P\,\theta_1}$$

$$K_3 = \frac{\theta_3}{P\theta_2} \qquad \qquad \qquad \dots(10.18)$$

and

$$K_n = \frac{\theta_n}{P\,\theta_{n-1}}$$

The magnitude of constant K_1 is very large as compared to the rest of the equilibrium constants. This is because the interaction between the adsorbate and adsorbent decreases very rapidly as the distance from the surface is increased. The difference between K_2 and K_3...etc. is generally much smaller than that between K_1 and K_2. As such it is assumed that

$$K_2 \cong K_3 \cong K_4 \dots\dots\cong K_n = K \qquad\qquad \dots(10.19)$$

were K is the equilibrium constant corresponding the saturated vapour–liquid equilibrium and is given as

$$\text{Saturated vapour} \rightleftharpoons \text{Liquid,}$$

then
$$K = 1/p_0 \qquad\qquad \dots(10.20)$$

where, P_0 is the equilibrium vapour pressure of the liquid. With the approximation given in Eq. (10.19), the various equilibrium constants of Eq. (10.18) may be represented as

$$K_1 = \frac{\theta_1}{P\theta_v}$$

$$K_2 \cong K = \frac{\theta_2}{P\,\theta_1} \qquad\qquad \dots(10.21)$$

$$K_3 \approx K = \frac{\theta_3}{P\theta_2}$$

$$\dots\dots\dots\dots\dots\text{and so on}$$

Rearranging the above expression and making use of Eq. (10.20), we have

$$\theta_1 = K_1 P \, \theta_v$$

$$\theta_2 = K P \theta_1 = \left(\frac{1}{P_0}\right) P (K_1 \, P \, \theta_v) = K_1 P \left(\frac{P}{P_0}\right)\theta_v$$

$$\theta_3 = K P \theta_2 = \left(\frac{1}{P_0}\right) P \left[K_1 \, P \left(\frac{P}{P_0}\right)\theta_v \right] = K_1 \, P \left(\frac{P}{P_0}\right)^2 \theta_v \qquad \left.\right\} \quad \ldots(10.22)$$

$$\ldots\ldots\text{and so on}$$

If it is assumed that the entire adsorbent surface is covered then the total coverage of the first layer will be given by

$$\theta_T = \theta_{total} = \theta_v + \theta_1 + \theta_2 + \ldots\ldots = 1 \qquad \ldots(10.23)$$

On substituting the value of θ_1, θ_2 ....etc from Eq. (10.22) into Eq. (10.23) we get

$$\theta_T = \theta_v + K_1 P \, \theta_v + K_1 P \left(\frac{P}{P_0}\right)\theta_v + K_1 P \left(\frac{P}{P_0}\right)^2 \theta_v + \ldots = 1$$

or

$$\theta_T = \theta_v \left[1 + K_1 P \left\{1 + \left(\frac{P}{P_0}\right) + \left(\frac{P}{P_0}\right)^2 + \ldots\right\}\right] = 1 \qquad \ldots(10.24)$$

since, $\frac{P}{P_0} \le 1$, we can write

$$\left\{1 + \left(\frac{P}{P_0}\right) + \left(\frac{P}{P_0}\right)^2 + \ldots\ldots\ldots\right\} = \left[1 - \left(\frac{P}{P_0}\right)\right]^{-1} = \frac{1}{1 - (P/P_0)} \qquad \ldots(10.25)$$

Hence from Eqs. (10.24) and (10.25), one can write

$$\theta_T = \theta_v \left[1 + \frac{K_1 P}{1 - (P/P_0)}\right] = 1$$

or

$$\theta_v = \frac{1}{1 + \frac{K_1 P}{\{1 - (P/P_0)\}}} = \frac{1 - (P/P_0)}{1 + K_1 P - (P/P_0)} \qquad \ldots(10.26)$$

Further, the total volume of the adsorbed gas (V) is given by

$$V = V_m \ (\theta_1 + 2\theta_2 + 3\theta_3 + \ldots\ldots\ldots) \qquad \ldots(10.27)$$

where V_m is the volume of the gas required for monolayer adsorption. Substituting the values of θ_1, θ_2, θ_3 ....from Eq. (10.22) into Eq. (10.27), we get

$$V = V_m \ K_1 P \ \theta_v \ \{1 + 2 \ (P/P_0) + 3 \ (P/P_0)^2 + \ldots\ldots\} \qquad \ldots(10.28)$$

But since

$$\left[1 + 2\left(\frac{P}{P_0}\right) + 3\left(\frac{P}{P_0}\right)^2 + \ldots\ldots\ldots\ldots \right] = \frac{1}{(1 - P/P_0)^2} \qquad \ldots(10.29)$$

therefore, the Eq.(10.28) simplifies as

$$V = V_m \ \frac{K_1 P \theta_v}{(1 - P/P_0)^2} \qquad \ldots(10.30)$$

Again on substituting the value of θ_v from Eq. (10.26) in to Eq. (10.30), we get

$$V = \frac{V_m \ K_1 \ P}{(1 - P/P_0) \ (1 + K_1 P - P/P_0)} \qquad \ldots(10.31)$$

The pressure P in Eq. (10.31) may be replaced in terms of relative pressure (P/P_0). For this one can write

$$P = P_0 \times \frac{P}{P_0}$$

and then with the help of Eq. (10.20), it may be written that

$$P = \frac{1}{K}\left(\frac{P}{P_0}\right) \qquad \ldots(10.32)$$

On substitution of Eq. (10.32) in Eq. (10.31) one obtains

$$V = \frac{V_m \ (K_1/K) \ (P/P_0)}{(1 - P/P_0) \left[1 + \left(\frac{K_1}{K}\right)\left(\frac{P}{P_0}\right) - \left(\frac{P}{P_0}\right)\right]} \qquad \ldots(10.33)$$

or

$$V = \frac{V_m C \ (P/P_0)}{(1 - P/P_0)\left[1 + C \left(\frac{P}{P_0}\right) - \left(\frac{P}{P_0}\right)\right]} \qquad \ldots(10.34)$$

where $C = K_1/K$ is a new constant. Eq. (10.34) is the well known Brunauer, Emmett and Teller (BET) equation applicable for multilayer adsorption of gaseous molecules. Equation (10.34) may be rearranged in the following manner:

$$\left(1 - \frac{P}{P_0}\right)\left[1 + C\left(\frac{P}{P_0}\right) - \left(\frac{P}{P_0}\right)\right] V = V_m \ C \ \frac{P}{P_0}$$

or

$$\frac{P \ P_0}{V(P_0 - P)} = \frac{1}{V_m} \frac{P_0}{C} + \frac{1}{V_m} \frac{(C-1)P}{C} \qquad \ldots(10.35)$$

or

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m} \frac{1}{C} + \frac{1}{V_m} \frac{(C-1)P}{CP_0} \qquad \ldots(10.36)$$

Eq. (10.36) is a general form of BET equation for multilayer adsorption of gases on solid adsorbent.

Thus, a plot of $\frac{P}{V(P_0 - P)}$ against $\left(\frac{P}{P_0}\right)$ should give a straight line whose intercept and slope are $\left(\frac{1}{V_m C}\right)$ and $\left(\frac{C-1}{V_m C}\right)$ respectively. The two constants V_m and C can thus be evaluated. Knowing the value of V_m, the surface area of the adsorbent can be determined.

Further, since $C = \frac{K_1}{K}$ and $K = \frac{1}{P_0}$

Therefore, $\quad C = \frac{K_1}{(1/P_0)} = P_0 K_1$

or $\quad K_1 = \frac{C}{P_0}$

On substituting the value of C in Eq. (10.35) one gets

$$\frac{PP_0}{V(P_0 - P)} = \frac{1}{V_m K_1} + \frac{1}{V_m} \frac{(P_0 K_1 - 1) \ P}{P_0 K_1} \qquad \ldots(10.37)$$

If P_0 is much greater than P, then $P_0 - P = P_0$ and $P_0K_1 - 1 \approx P_0K_1$

Thus,
$$\frac{P}{V} = \frac{1}{V_m}\frac{1}{K_1} + \frac{P}{V_m}$$
...(10.38)

This Eq. (10.38) is identical to the Langmuir adsorption isotherm Eq. (10.14).

1. What do you understand by adsorption? Define the terms used in adsorption phenomena.

2. Distinguish between physisorption and chemisorption.

3. What do you understand by adsorption isotherm and how many type of isotherms are known?

4. What is Freundlich adsorption isotherm? Derive it.

5. What do you understand by Langmuir adsorption isotherm? Derive the equation on the basis of thermodynamic and kinetic considerations.

6. Derive BET equation for multilayer adsorption on solid surface and how can surface area be determined with the help of BET equation?

Surface films

The compositions of surface layers have been investigated by the simple but technically elegant procedure of slicing thin layers off the surfaces of solutions and analysing their compositions. The physical properties of surface films have also been investigated. Surface films one molecule thick are called **monolayers**. When a monolayer has been transferred to a solid support, it is called a **Langmuir–Blodgett film**, after Irving Langmuir and Katherine Blodgett, who developed experimental techniques for studying them.

(a) Surface pressure

The principal apparatus used for the study of surface monolayers is a **surface film balance** (Fig. 17.27). This device consists of a shallow trough and a barrier that can be moved along the surface of the liquid in the trough, and hence compress any monolayer on the surface. The **surface pressure,** π, the difference between the surface tension of the pure solvent and the solution ($\pi = \gamma^* - \gamma$) is measured by using a torsion wire attached to a strip of mica that rests on the surface and pressing against one edge of the monolayer. The parts of the apparatus that are in touch with liquids are coated in polytetrafluoroethene to eliminate effects arising from the liquid–solid interface. In an actual experiment, a small amount (about 0.01 mg) of the surfactant under investigation is dissolved in a volatile solvent and then poured on to the surface of the water; the compression barrier is then moved across the surface and the surface pressure exerted on the mica bar is monitored.
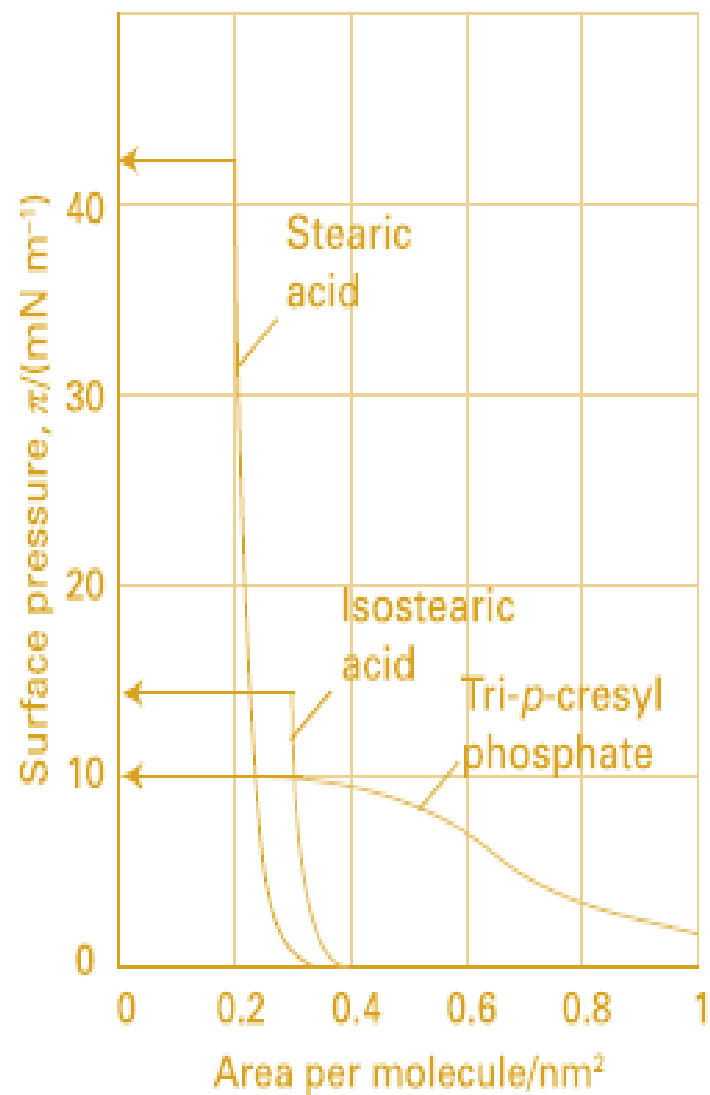
Fig. 17.28 The variation of surface pressure with the area occupied by each surfactant molecule. The collapse pressures are indicated by the horizontal arrow.

Some typical results are shown in Fig. 17.28. One parameter obtained from the isotherms is the area occupied by the molecules when the monolayer is closely packed. This quantity is obtained from the extrapolation of the steepest part of the isotherm to the horizontal axis. As can be seen from the illustration, even though stearic acid (**15**) and isostearic acid (**16**) are chemically very similar (they differ only in the location of a methyl group at the end of a long hydrocarbon chain), they occupy significantly different areas in the monolayer. Neither, though, occupies as much area as the tri-*p*-cresyl phosphate molecule (**17**), which is like a wide bush rather than a lanky tree.

The second feature to note from Fig. 17.28 is that the tri-*p*-cresyl phosphate isotherm is much less steep than the stearic acid isotherms. This difference indicates that the tri-*p*-cresyl phosphate film is more compressible than the stearic acid films, which is consistent with their different molecular structures.

A third feature of the isotherms is the **collapse pressure**, the highest surface pressure. When the monolayer is compressed beyond the point represented by the collapse pressure, the monolayer buckles and collapses into a film several molecules thick. As can be seen from the isotherms in Fig. 17.28, stearic acid has a high collapse pressure, but that of tri-*p*-cresyl phosphate is significantly smaller, indicating a much weaker film.

15 Stearic acid, $C_{17}H_{35}COOH$

16 Isostearic acid, $C_{17}H_{35}COOH$

the interface between hydrophilic and hydrophobic phases. A surfactant accumulates at the interface, and modifies its surface tension and hence the surface pressure. To establish the relation between the concentration of surfactant at a surface and the change in surface tension it brings about, we consider two phases α and β in contact and suppose that the system consists of several components J, each one present in an overall amount n_J. If the components were distributed uniformly through the two phases right up to the interface, which is taken to be a plane of surface area σ, the total Gibbs energy, G, would be the sum of the Gibbs energies of both phases, $G = G(\alpha) + G(\beta)$. However, the components are not uniformly distributed because one may accumulate at the interface. As a result, the sum of the two Gibbs energies differs from G by an amount called the **surface Gibbs energy, $G(\sigma)$**:

$$G(\sigma) = G - \{G(\alpha) + G(\beta)\}$$
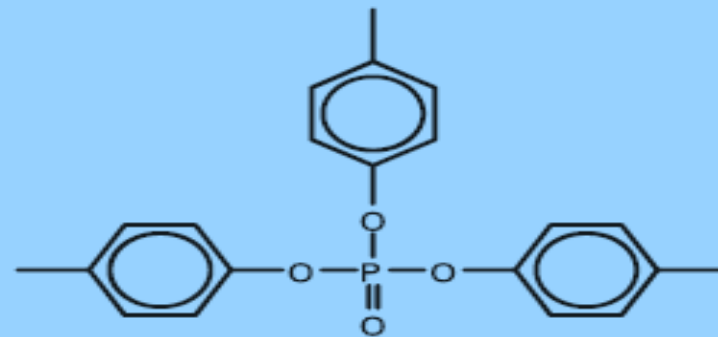
> Definition of surface Gibbs energy

[17.45]

Similarly, if it is supposed that the concentration of a species J is uniform right up to the interface, then from its volume we would conclude that it contains an amount $n_J(\alpha)$ of J in phase α and an amount $n_J(\beta)$ in phase β. However, because a species may accumulate at the interface, the total amount of J differs from the sum of these two

17 Tri-p-cresylphosphate

amounts by $n_J(\sigma) = n_J - \{n_J(\alpha) + n_J(\beta)\}$. This difference is expressed in terms of the surface excess, Γ_J:

$$\Gamma_J = \frac{n_J(\sigma)}{\sigma}$$

Definition of surface excess [17.46]

The surface excess may be either positive (an accumulation of J at the interface) or negative (a deficiency there).

The relation between the change in surface tension and the composition of a surface (as expressed by the surface excess) was derived by Gibbs. In the following *Justification* we derive the Gibbs isotherm, between the changes in the chemical potentials of the substances present in the interface and the change in surface tension:

$$d\gamma = -\sum_J \Gamma_J d\mu_J$$

Gibbs isotherm (17.47)

Justification 17.7 *The Gibbs isotherm*

A general change in G is brought about by changes in T, p, and the n_J:

$$dG = -S\,dT + V\,dp + \gamma\,d\sigma + \sum_J \mu_J\,dn_J$$

When this relation is applied to G, $G(\alpha)$, and $G(\beta)$ we find

$$dG(\sigma) = -S(\sigma)dT + \gamma\,d\sigma + \sum_J \mu_J\,dn_J(\sigma)$$

because at equilibrium the chemical potential of each component is the same in every phase, $\mu_J(\alpha) = \mu_J(\beta) = \mu_J(\sigma)$. Just as in the discussion of partial molar quantities (Section 5.1), the last equation integrates at constant temperature to

$$G(\sigma) = \gamma\sigma + \sum_J \mu_J n_J(\sigma)$$

We are seeking a connection between the change of surface tension $d\gamma$ and the change of composition at the interface. Therefore, we use the argument that in Section 5.1 led to the Gibbs–Duhem equation (eqn 5.12b), but this time we compare the expression

$$dG(\sigma) = \gamma\,d\sigma + \sum_J \mu_J\,dn_J(\sigma)$$

(which is valid at constant temperature) with the expression for the same quantity but derived from the preceding equation:

$$dG(\sigma) = \gamma\,d\sigma + \sigma\,d\gamma + \sum_J \mu_J\,dn_J(\sigma) + \sum_J n_J(\sigma)d\mu_J$$

The comparison implies that, at constant temperature,

$$\sigma \, d\gamma + \sum_J n_J(\sigma) d\mu_J = 0$$

Division by σ then gives eqn 17.47.

··

Now consider a simplified model of the interface in which the 'oil' and 'water' phases are separated by a geometrically flat surface. This approximation implies that only the surfactant, S, accumulates at the surface, and hence that Γ_{oil} and Γ_{water} are both zero. Then the Gibbs isotherm equation becomes

$$d\gamma = -\Gamma_S \, d\mu_S \qquad (17.48)$$

For dilute solutions,

$$d\mu_S = RT \ln c \qquad (17.49)$$

where c is the molar concentration of the surfactant. It follows that

$$d\gamma = -RT\Gamma_S \frac{dc}{c}$$

at constant temperature, or

$$\left(\frac{\partial \gamma}{\partial c}\right)_T = -\frac{RT\Gamma_S}{c} \qquad (17.50)$$

If the surfactant accumulates at the interface, its surface excess is positive and eqn 17.50 implies that $(\partial \gamma / \partial c)_T < 0$. That is, the surface tension decreases when a solute accumulates at a surface. Conversely, if the concentration dependence of γ is known, then the surface excess may be predicted and used to infer the area occupied by each surfactant molecule on the surface.